Low-Cost Real-Time Gas Monitoring Using a Laser Plasma Induced by a Third Harmonic Q-Switched Nd-YAG Laser

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Abstract. A gas plasma induced by a third harmonic Nd-YAG laser with relatively low pulsed energy (about 10 mJ) has favorable characteristics for gas analysis due to its low background characteristics, nevertheless a high power fundamental Nd-YAG laser (100-200 mJ) is widely used for laser gas breakdown spectroscopy. The air plasma can be used as a low-cost real-time gas monitoring system such that it can be used to detect the local absolute humidity, while a helium plasma can be used for gas analysis with a high level of sensitivity. A new technique using a helium plasma to improve laser ablation emission spectroscopy is proposed. Namely, the third harmonic Nd-YAG laser is focused at a point located some distance from the target in the 1-atm helium surrounding gas. By using this method, the ablated vapor from the target is excited through helium atoms in a metastable state in the helium plasma.

Keywords: *third harmonic Nd-YAG laser; air plasma; He plasma; He metastable state; gas monitoring; gas analysis*.

1 Introduction

Laser induced plasma spectroscopy (LIPS) has been widely used for the elemental analysis of a solid, since it represents a rapid quantitative technique without the need for sample pretreatment. The flexibility of this technique can be applied not only to solids but also to liquids and gases. Cremers and Radziemski [1] applied LIPS, for the first time, for the analysis of chlorine and

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fluorine in air. For plasma generation, they used a Q-switched fundamental Nd-YAG laser, and for the spectral measurement, they used a gated OMA to cut off the strong continuous spectrum that appears during the initial stage of the laser plasma generation in the gas. Compared to conventional techniques currently used in gas analysis, such as mass spectrometry and chromatography, the LIPS technique has many advantages, including its use in real time in situ analysis, and the need for only a small amount material for the analysis.

However, a number of papers have been published on gas analysis, and in most of these, a fundamental Nd-YAG laser was used as in the case of Cremer and Radziemski's study. In order to generate a stable gas plasma using a fundamental Nd-YAG laser, at least 100 mJ pulse energy is required. Consequently, the resulting plasma is rather large in size and a high heat capacity is maintained in the plasma. Such a plasma represents a source of fire in the air, which contains a burning gas such as fuel gas, benzene, acetone and ethanol. Therefore, the fundamental Nd-YAG laser is not applicable for use as a gas monitoring system under such conditions.

In order to overcome this problem, we used a third harmonic Nd-YAG laser (355 nm) as the exciting light source for generating a plasma in gases. By employing this UV laser, the threshold for plasma generation in a gas reaches as low as a few mJ, and at 10 mJ, the plasma is already very stable. This is because the multiphoton ionization process takes place with a much higher probability than that for a fundamental one. [2] The resulting plasma is much smaller in size, has a low heat capacity in the plasma, and this type of plasma has less probability of initiating a fire, even when the air plasma contains a burning gas.

It is also noteworthy that, by employing a third harmonic UV laser, a low cost gas monitoring system can be constructed for industrial or environmental monitoring with the aid of inexpensive CCD detectors instead of the expensive gated OMA required for the fundamental Nd-YAG laser, because the plasma induced by the low energy third harmonic Nd-YAG laser has a relatively low background emission spectrum compared to that for a fundamental Nd-YAG laser.

As a result of our study, we propose a new method for laser ablation emission spectrochemical analysis. In this method, the vapor of ablated atoms is indirectly excited through collision with metastable He atoms which are produced by focusing the third harmonic Nd-YAG laser in front of the target placed in ambient He gas.

2 Experimental procedure

Figure 1 shows the experimental set up used in this experiment. A Q-switched Nd-YAG laser (Surelite lasers Continuum, model 811U-06) with a pulse duration of 7 ns was operated at 355 nm (third harmonic oscillation) with a repetition frequency of 10 Hz. The laser beam was focused through a quartz window in a gas chamber by a lens (f = 70 mm) to form the micro gas breakdown plasma. The chamber was constructed of an acrylic plate (10 cm x 5 cm x 7 cm), and equipped with a gas inlet and outlet for gas flow and two other quartz windows to observe the plasma emission.

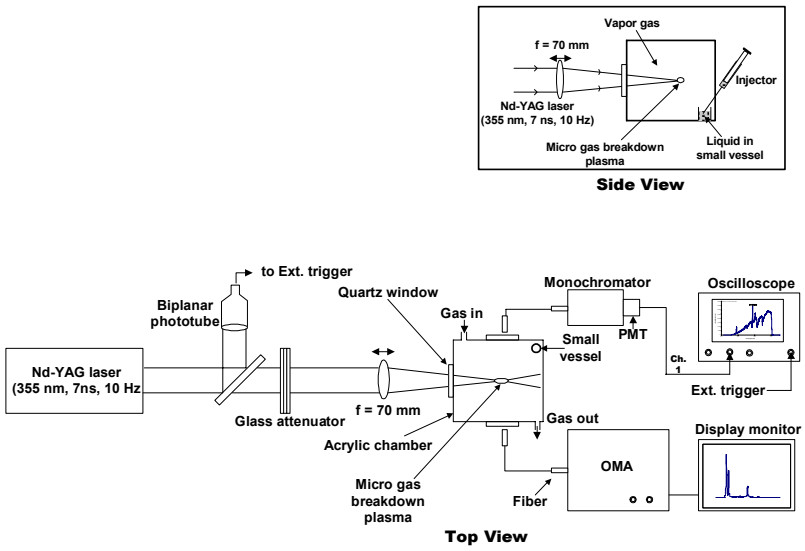

Figure 1 Experimental setup used for gas monitoring and gas analysis. The inset shows the method used to introduce a liquid into the vessel in the chamber.

As shown in the inset of Fig.1, a small vessel with a diameter of 10 mm was placed in the corner of the chamber, and according to experimental need, the liquid was poured into the vessel with the aid of an injector through a small hole in the chamber so that gas vapor will naturally spreads. The room temperature was fixed at 23 ^{0}C. The atoms in the vapor gas are excited by the micro gas breakdown plasma and its emission was collected by an optical fiber and fed into the optical multichannel analyzer (OMA). The OMA (Atago Macs-320) consists of a 320 mm-focal length spectrograph with a grating of 1,200 groves/mm for high resolution, a 1,024 channel photodiode detector array and a micro-channel plate image intensifier. The spectral range covered by this OMA is 50 nm. To measure the time profile of the emission, another optical fiber was used and one of its ends was fixed in front of the slit of a monochromator

(Nikon P-250). The optical signal was detected by a fast photomultiplier tube (PMT) (Hamamatsu, R7400U-04; rise time of 0.78 ns) and fed into a digital oscilloscope (HP 5461B). The oscilloscope was triggered by a part of the Nd-YAG laser light with the aid of a biplanar phototube (Hamamatsu, R1193U-51).

In a comparative study, we also ran a gas analysis experiment using a fundamental Nd-YAG laser (Quanta Ray, GCR-12S, 8 ns) in another laboratory and the emission spectrum was obtained using a separate OMA system, which has a slightly lower resolution (Princeton instrument IRY-700 attached to a spectrograph of focal length 150 mm). The spectral range covered by this OMA is 80 nm. The OMA was operated in the time-integrated mode in all cases.

3 Results and discussion

In order to demonstrate the gas analysis, the carbon emission line was observed after the injection of ethanol into the vessel placed in the chamber. Fig.2(a) shows the emission spectrum of carbon taken when a 355 nm laser pulse of 10 mJ was focused in clean air containing ethanol as the impurity gas, which was generated 5 minutes after the injection of the ethanol. A strong carbon emission line (C I 247.8 nm), one of the constituents of the ethanol molecule, can be clearly seen. This carbon line increases with time. Fig.2(b) shows the carbon emission line produced by focusing 130 mJ of the fundamental Nd-YAG laser light in clean air containing ethanol under the same conditions, namely 5 minutes after injection. In this case, the carbon emission line is weak compared to the continuous background emission intensity. This result indicates that the third harmonic Nd-YAG laser light is superior to the fundamental Nd-YAG laser for gas analysis, and by combining it with the OMA system without a gating, a low cost compact gas monitoring system can in practice, be constructed. This experiment proves that, except for the C line (C I 247.8nm), other atomic lines such as H (H I 656.2 nm) and O (O I 777.2 nm) are easily detected.

In order to determine if a qualitative gas analysis can be achieved, the emission ratio between C and H was observed for several types of organic compounds by changing the gas concentration in the clean air. Fig.3 shows the correlation between the C and H emission for benzene (C_6H_6), ethanol (C_2H_5OH) and acetone (CH_3COCH_3) in the vapor state. The gas concentration naturally increases with time after these liquids were poured into the vessel using an injector, and the C and H emission intensities were periodically measured with time. It can be seen that each curve has a linear relationship between C emission intensity and H emission intensity. This indicates that the characteristics of the plasma and the excitation process of the C and H atoms remain constant regardless of the range of the impurity gas pressure investigated. If the plasma

characteristic or excitation process changes when the impurity gas pressure is varied, the emission intensity ratio between C and H would also be changed. It should also be noted that the slopes of the acetone and ethanol curves are nearly the same, but are higher than that for benzene. The atomic ratio of C and H in ethanol, acetone and benzene are 1:3, 1:2, and 1:1, respectively. Based on this ratio, the slope for ethanol should be three times greater than that for benzene. However, the slopes are actually only 1.5 times greater. This is probably due to the difference in the mechanism of dissociation of molecules to atoms. It is postulated that, in the case of benzene, the direct dissociation process plays in the multiphoton absorption of the 355 nm laser light, while for ethanol and acetone, the molecules would be dissociated via a thermal process in the hot plasma. [3]

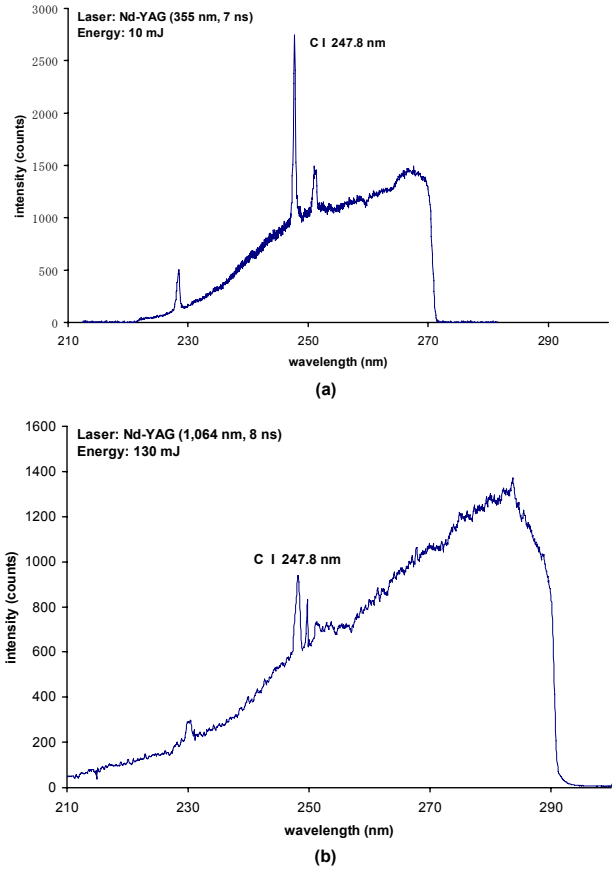

Figure 2 Time integrated emission spectrum of C I 247.8 nm obtained for ethanol vapor. Data in (a) were obtained by third harmonic Nd-YAG laser of 10 mJ; and in (b) were obtained by fundamental Nd-YAG laser of 130 mJ. Both data were obtained in clean air containing ethanol vapor as impurity gas.

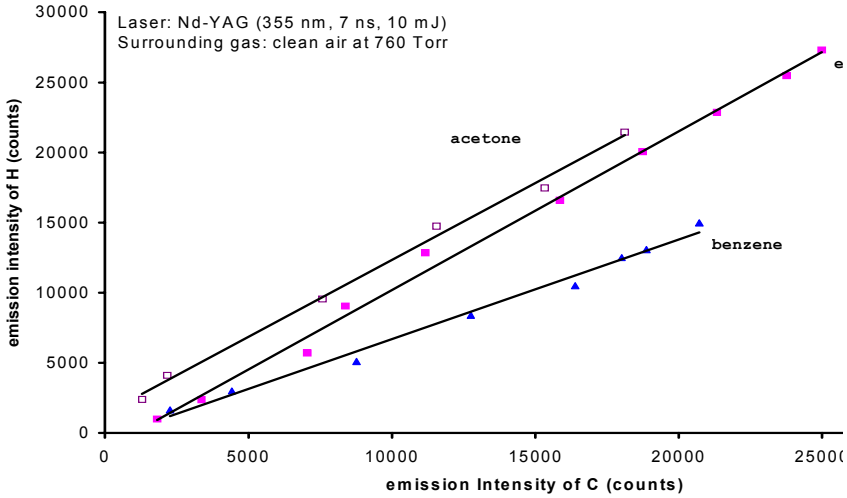

Figure 3 Correlation between the emission intensity of C and that of H obtained from vaporized benzene, ethanol and acetone.

Based on the result shown in Fig.3, the emission ratio of C and H is not always proportional to the C/H ratio in the molecule. Therefore, this result cannot be used for the accurate identification of a specific organic molecule. However, the method is still useful for a gas monitoring system. This is because, in gas monitoring applications, if the C and H emission line suddenly increases in the emission spectrum, it indicates that organic gas is clearly entered in the micro gas plasma region.

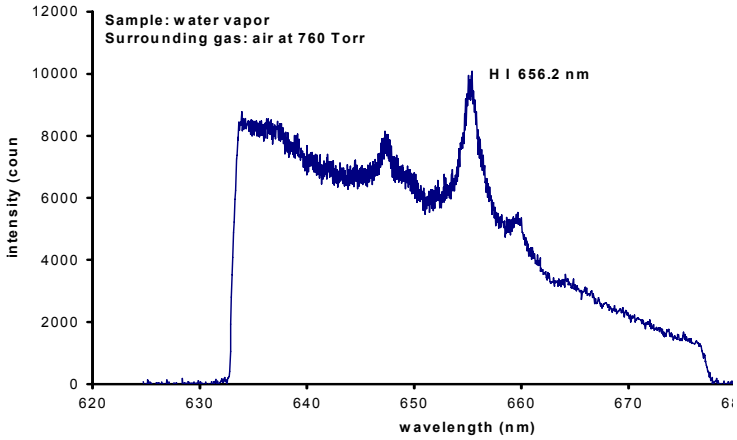

Figure 4 Emission spectrum of H obtained when a laser pulse of 10 mJ was focused on air. Temperature and humidity were 23 ^{0}C and 74%, respectively.

It is usually very difficult to measure the local humidity with a high precision and with a fast response, namely a real-time measurement. In an ordinary humidity meter, the measurement is indirectly made using a sensor, the characteristics of which change due to the attachment of water molecules to the surface. Therefore, the reliability of the measurement is relatively low with considerable error. One method for measuring the absolute value of H_2O contained in air by an optical method is the use of infrared absorption spectroscopy [4]. However, this method cannot be applied to the measurement of humidity at a local point. It is generally believed that the hydrogen emission intensity observed from the laser plasma is proportional to the amount of H_2O in the air, and the laser plasma produced by the 355 nm Nd-YAG laser can be successfully applied to measure the local absolute humidity, because as described above, the plasma is very small in size and very stable. Fig. 4 shows the emission spectrum of H I 656.2 nm when a laser pulse of 10 mJ was focused in the air of a room at a temperature and humidity of 23 ^{0}C and 74%, respectively.

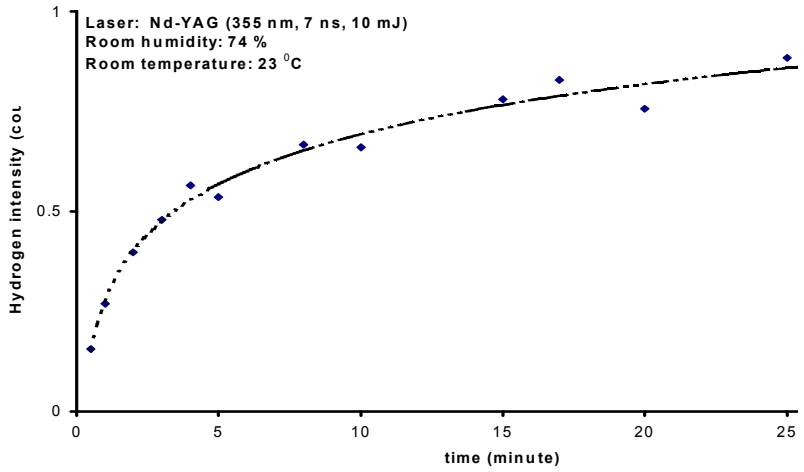

Figure 5 The growth of H emission intensity in air as a function of time.

An experiment was conducted to demonstrate the possibility of humidity measurement in real-time. Namely, the H emission was measured as a function of time after water was added by an injector into the vessel contained by the chamber containing clean air. Fig.5 shows the H emission intensity observed from the plasma as a function of time. It can be seen that the features of the curve, namely the initial growth and saturation, coincide with those expected for the water vapor pressure under such conditions.

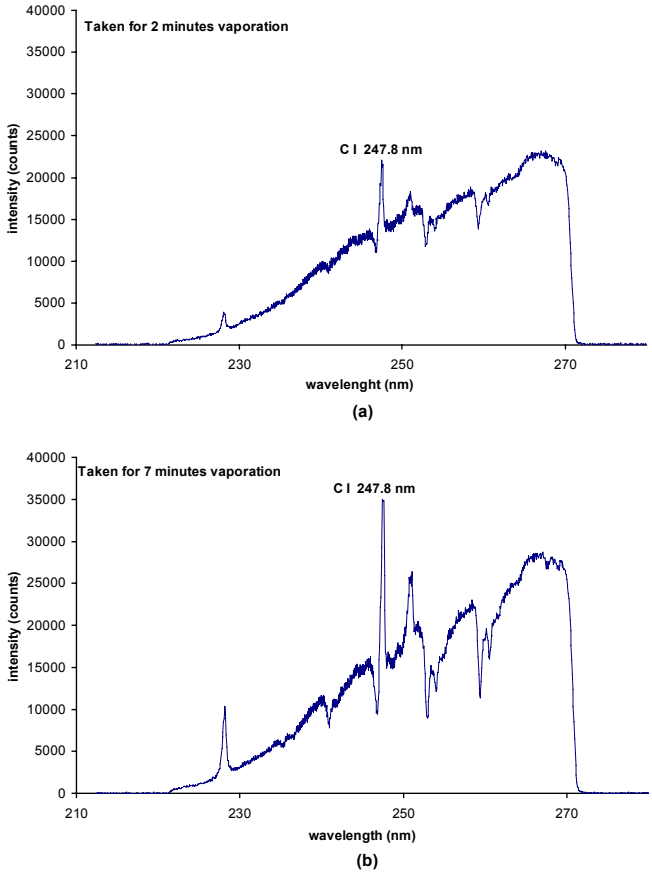

Figure 6 The absorption spectrum of benzene obtained when 10 mJ of a 355 nm YAG laser was focused in a cell containing benzene vapor in air. The spectrum was obtained 2 minutes after injection (a) and a spectrum obtained at 7 minutes (b).

We also found an interesting phenomenon regarding the laser plasma. Namely, for some molecules, which have a non-broading vibrational structure, such as benzene, a gas analysis can be made by an absorption spectroscopy using the laser plasma as the light source for absorption. Fig.6 shows the absorption spectrum observed when 10 mJ of the third harmonic Nd-YAG laser was focused in the chamber after liquid benzene was poured into the vessel; (a) was obtained at 2 minutes, and (b) was obtained at 7 minutes after the injection. In Fig. 6(a), it can be seen that, in addition to the C emission line, some dips are evident, due to absorption. This signal becomes much more clear in Fig.6(b). The wavelength of each dip completely coincides with those of the benzene absorption spectrum [5].

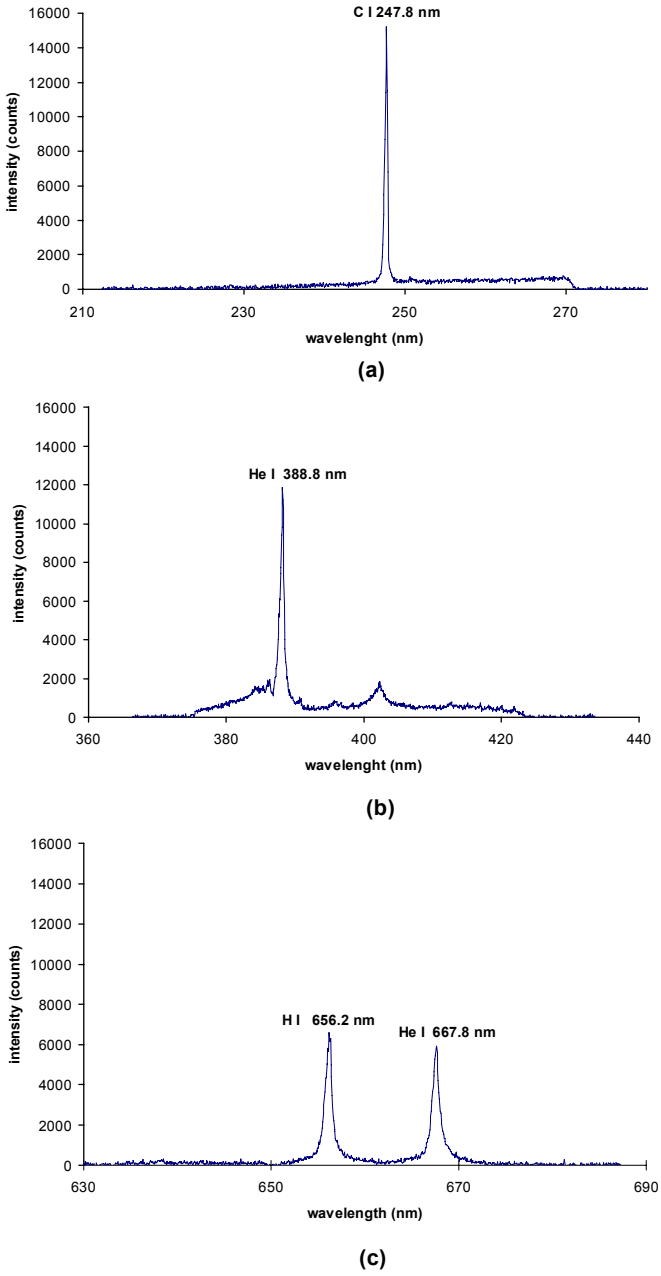

Figure 7 The emission spectra obtained from acetone vapor 5 minutes after the injection of liquid acetone into the vessel in three different wavelength ranges; 210 nm-270 nm (a); 360 nm- 440 nm (b); and 630 nm-690 nm (c). All data were taken when the third harmonic Nd-YAG laser of 50 mJ was focused in surrounding He gas.

As described above, the air plasma produced by the third harmonic Nd-YAG laser is small in size but high in brightness with a nearly continuous emission spectrum in the UV region. Therefore, this plasma is suitable as a light source for absorption spectroscopy. If the imaging method is employed, in which the air plasma image is projected on the entrance slit of the monochromator, so as to effectively collect the emission from the air plasma, the emission spectrum of the plasma can be obtained with the dips due to the benzene absorption even when the distance between the plasma and detector is intentionally extended. Using this method, it is possible to analyze gaseous benzene with a high degree of sensitivity.

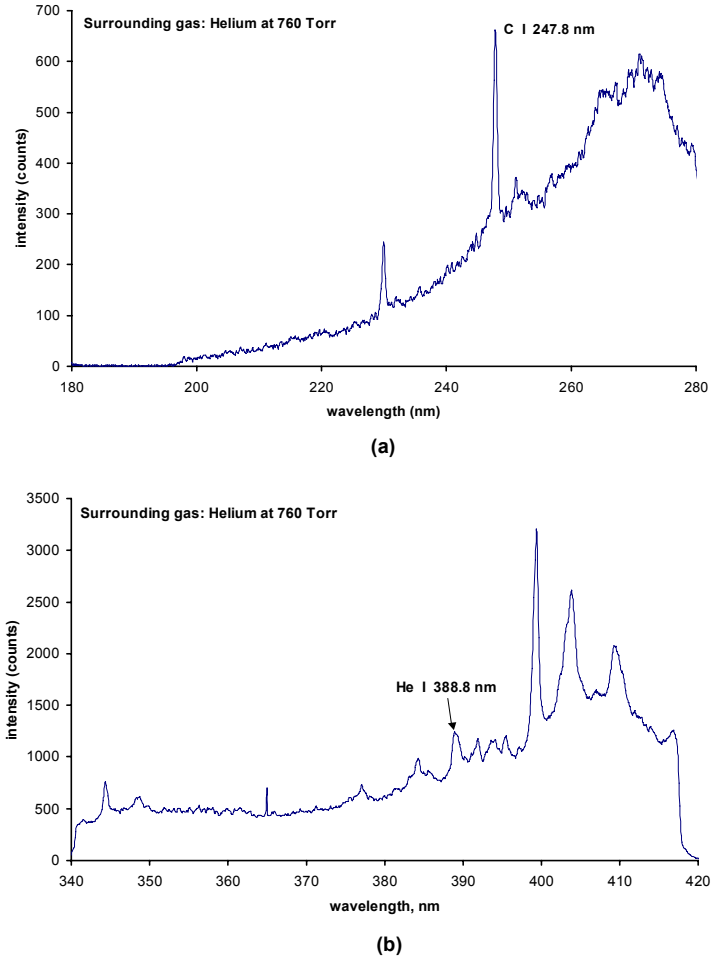

Figure 8 The emission spectra of C I 247.8 nm (a) and He 567.3 nm (b) taken 5 minutes after the injection of ethanol in vessel by focusing fundamental Nd-YAG laser of 130 mJ.

As Michael et al. proved in an experiment where a gas plasma induced by a fundamental Nd-YAG laser [6], the spectrum background can be reduced using He gas in place of air. In our study, we used the third harmonic Nd-YAG laser in place of the fundamental Nd-YAG laser. Therefore, it would be expected that the background would be suppressed to a much greater extent for the third harmonic one.

The emission spectrum of the gas plasma was investigated by focusing the third harmonic Nd-YAG laser at 50 mJ into He gas containing acetone as the impurity. Although the threshold energy of the laser light for inducing the plasma in the He gas is 9 mJ (in air, it is 2 mJ), an energy of 50 mJ was selected to obtain a sufficient signal for the emission spectrum. Fig.7 shows the spectrum obtained 5 minutes after the injection of the acetone in the vessel in three different spectral wavelength ranges, 210 nm-270 nm (a); 360 nm- 440 nm (b) and 630 nm-690 nm (c). As shown in (a), a strong C I 247.8 nm emission line is observed with a very low background spectrum. It should be noted that the He neutral emission lines of He I 388.8 nm and of He I 667.8 nm are strong as shown in (b) and (c), respectively. It should also be noted that, a strong H emission lines of 656.2 nm is observed with a relatively narrow spectral width and with a very low background spectrum compared to those for Fig.4.

In order to compare these techniques, the fundamental Nd-YAG laser of 130 mJ was focused in He gas containing ethanol as an impurity. Fig.8 shows the spectrum obtained 5 minutes after the injection of the ethanol into the vessel. In this experiment, we used a different OMA with a slightly lower resolution. It can clearly be seen that the spectral features are quite different from those observed for the third harmonic Nd-YAG laser. Nevertheless, the C line is clearly detected as shown in (a), and the spectral background is very high compared to the case of He. It should also be noted that the He emission line is very low as shown in (b). From these results, we assumed that the excitation of an atom in the He gas plasma induced by the third harmonic Nd-YAG laser is different from that induced by the fundamental laser and it is also different from the air plasma induced by the third harmonic one.

In order to clarify the mechanism of atomic excitation in the He gas plasma, we examined the time profile of the atomic emission lines. Fig.9(a) shows how the He I 587.6 nm emission intensity changes with time. It can be seen that the rise time of the emission is rather long, about 100 ns, and decays slowly until about 2 μs. As shown in (b), the emission of H consists of two components, namely a spiky emission which occurs just after the laser bombardment while the other has a long decay time, which nearly coincides with the He emission. For the sake of comparison, the time profile for the H emission was also obtained using air containing acetone as an impurity. As shown in Fig.9(c), the emission rise

time and decay time are very fast and quite different compared to the case of He.

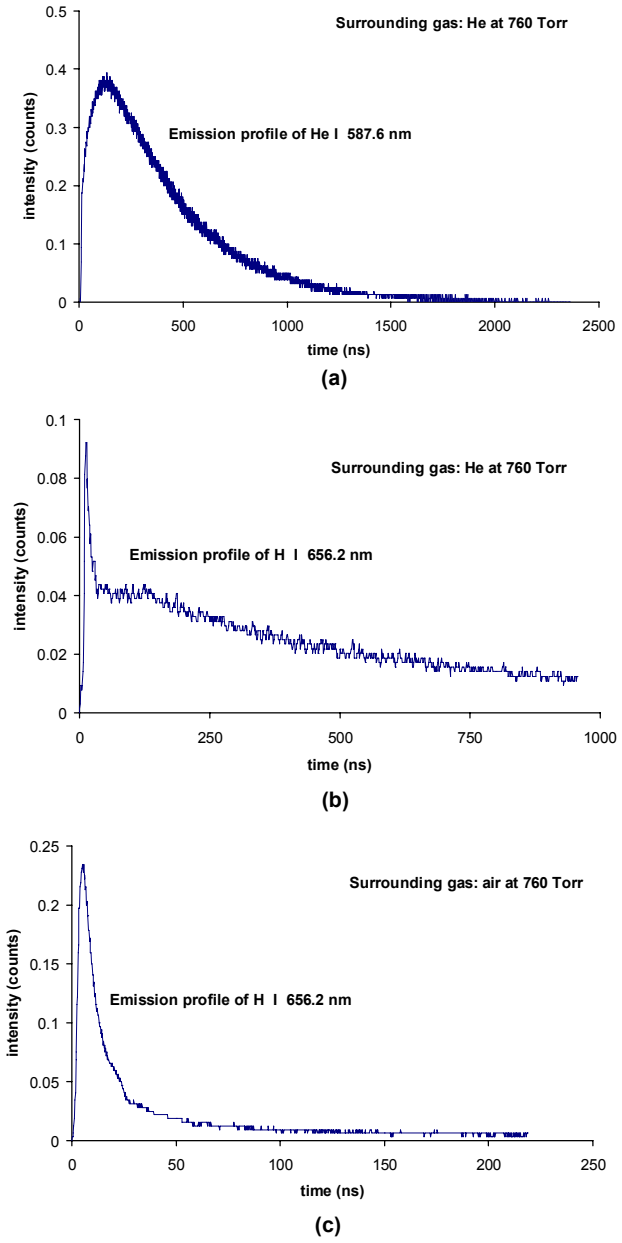

Figure 9 Time profile of atomic emission induced by a third harmonic Nd-YAG laser. He emission in the surrounding He gas (a), H emission in the surrounding He gas (b), and H emission in the surrounding air gas (c).

It is assumed that, in the He plasma induced by the low energy third harmonic laser, energy is conserved in the plasma mainly in the form of metastable He atoms (excitation energy is 19.8 eV) after the laser pulse is completed, while for the air plasma, the remaining energy is mainly in the form of the kinetic energy of atoms that form an explosive shock wave. One of the possible mechanisms to explain the long life of the He I 587.6 nm emission is that two metastable atoms collide leading to the formation of a He ion and electron, and that the excitation state for the He I 587.6 nm (23 eV) emission is produced through the recombination of these particles. It is also assumed that impurity atoms in the He plasma are excited by colliding with the metastable He. As is well known in He ICP (inductively coupled plasma), in which energy is supplied through a high frequency electric field, He in the metastable state, plays an important role in exciting impurity atoms. In contrast to this, in our He plasma, the He metastable state is optically produced using the UV laser. Based on the experimental results described above we conclude that the He plasma has considerable potential for use in gas analysis.

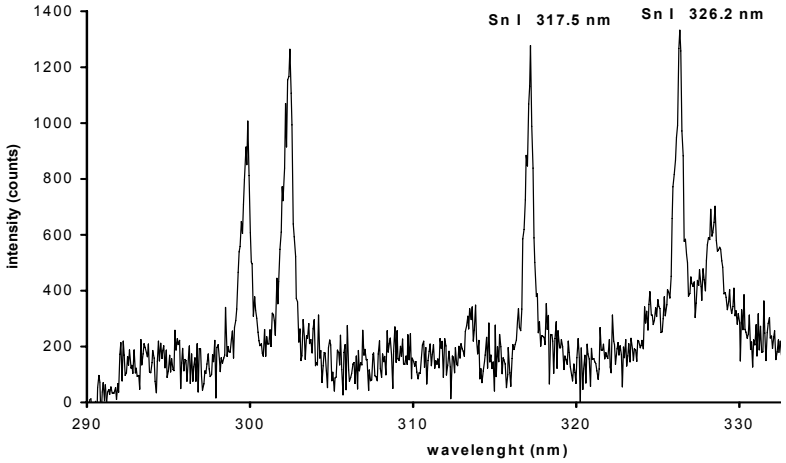

Figure 10 The spectrum of Sn observed when a third harmonic Nd-YAG laser is focused in He gas containing ablated vapor from a solder target.

Another interesting application of the He plasma induced by the third harmonic Nd-YAG laser is its combined use with a laser ablation technique. Namely, the laser light is focused at a point located some distance from the target placed in the surrounding He gas at 1 atm. With this configuration, the vapor of the ablated atoms from the target is effectively excited in the He plasma, as was observed in the gas analysis using the He plasma. For this purpose, two lasers are required, one for ablation and another, the third harmonic Nd-YAG laser, for producing a He plasma. In a preliminary experiment, we used one laser in

the method described as follows: first, in the cell used for the gas analysis, a Sn-Pb alloy rod was inserted during the laser irradiation so that the sample surface was at the laser focusing point and remained there for several seconds to undergo laser ablation. The rod sample was then removed from the focusing point. However, around the focusing point, the vapor of ablated atoms remained as an impurity gas. Thus the ablated atoms are excited in the He plasma through metastable He atoms. Fig.10 shows one of the results of this method, where a Sn-Pb alloy rod was used as the sample. It is seen that the Sn I 317.5 nm and Sn I 326.2 nm emission lines can be clearly observed with a low background emission. If we employ two lasers, one for the He plasma and the other for ablation, the atomic emission signal will be significantly improved. The best advantage of this method is its ability to sufficiently suppress the spectral background, because atoms are excited through the metastable He. In contrast to this, in ordinary laser ablation spectroscopy using a target plasma, a strong continuous emission takes place just above the surface due to the propelling of a strong shock wave [7-8]

Another advantage of this method is that, not only a hard sample, but a soft sample as well can be analyzed. As we reported in our previous papers [8-9] the shock wave plays an important role in exciting atoms in the target plasma. Based on this reason for a soft sample, the emitting plasma cannot be produced due to the lack of a repulsive force to induce the shock wave [10-11]. However, the ablation of atoms takes place with a rather low speed, producing a gas vapor from the target, and this vapor can be excited by the He plasma. In fact, the emission of Ca was clearly detected when a leaf was used in place of the solder, because a leaf contains considerable amounts of Ca.

4 Conclusion

A micro gas plasma is produced when a third harmonic Nd-YAG laser of 10 mJ is focused in air containing an impurity such as ethanol, acetone or benzene. Due to the fact that the spectrum obtained by the third harmonic Nd-YAG laser is very stable with a low background compared to the fundamental case, an inexpensive OMA without a gating can be employed to obtain the spectrum. Thus, this plasma can be used as a low cost gas monitoring system. As one example of a gas monitoring system, a real time local absolute humidity measurement was demonstrated. For benzene as an impurity in air, the benzene absorption spectrum can be observed in the plasma emission spectrum with a clear vibrational structure. Here the laser plasma functions as a high brightness light source for the absorption spectroscopy. It was also shown that the metastable excited state of helium atom can be utilized to induce delayed excitation of the ablated target atoms and thereby increasing the emission efficiency of the ablated atoms. It is further demonstrated that for Sn-Pb alloy

sample, high sensitive spectrochemical analysis of Sn can be realized by a newly introduced double excitation technique

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References

1. Cremers, D. A. & Radziemski, L. J., *Detection of chlorine and fluorine in air by laser-induced breakdown spectrometry*, Anal.Chem. **55** (1983) 1252-1256.
2. Radziemski, L. J. & Cremers, D. A., *Laser-Induced Plasmas and Applications* (Marcel Dekker Inc, New York and Basel, 1989) p.318.
3. Lewis, I. R. & Edwards, H. G. M., *Handbook of Raman Spectroscopy, from the Research Laboratory to the Process Line* (Marcel Dekker Inc, New York and basel, 2001) p. 307.
4. Svanberg, S., *Atomic and molecular spectroscopy* (Springer-Verlag, Berlin, 1992) p.242.
5. Jaffe, H. H., Orchin, M., *Theory and applications of ultraviolet spectroscopy* (John Wiley & Sons, 1962) p. 299.
6. Tran, M., Smith, B. W., Hahn, D. W. & Winefordner, J. D., *Detection of gaseous and particulate fluorides by laser-induced breakdown spectroscopy*, Appl.Spectrosc. **55** (2001) 1455- 1461.
7. Kagawa, K., Kawai, K., Tani, M., Kobayashi, T., *XeCl excimer laser-induced shock wave plasma and its application to emission spectrochemical analysis*, Appl.Spectrosc. **48** (1994) 198-205.
8. Marpaung, A. M., Hedwig, R., Pardede, M., Lie, T. J., Tjia, M. O., Kagawa, K., Kurniawan, H., *Shock wave plasma induced by TEA CO_2 laser bombardment on glass samples at high pressures*, Spectrochim.Acta **B55** (2000) 1591-1599.
9. Kurniawan, H., Kagawa, K., Okamoto, M., Ueda, M., Kobayashi, T., Nakajima, S., *Emission spectrochemical analysis of glass containing Li and K in high concentration using a XeCl excimer laser-induced shock wave plasma*, Appl.Spectrosc. **50** (1996) 299-305.
10. Suliyanti, M. M., Hedwig, R., Kurniawan, H., Kagawa, K., *The role of sub-target in the transversely excited atmospheric pressure CO_2 laser-induced shock-wave plasma*, Jpn.J.Appl.Phys. **37** (1998) 6628-6632.
11. Kagawa, K., Lie, T. J., Hedwig, R., Abdulmajid, S. N., Suliyanti, M. M., Kurniawan, H., *Sub target effect on laser plasma generated by*

transversely excited atmospheric CO_2 laser at atmospheric gas pressure, Jpn.J.Appl.Phys. **39** (2000) 2643-2646.